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ARSENOMOLYBDIC ACID AS AN  
ALKALOIDAL REAGENT

BY

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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## Arsenomolybdic Acid as an Alkaloidal Reagent

### I

#### Introduction

It has been the purpose of this work to prepare arsenomolybdic acid, to determine its formula, and to investigate its value as an alkaloidal precipitant.

Work on arsenomolybdic acid as an alkaloidal reagent is not found in the literature to date. However, Seyberth<sup>1</sup> gives the preparation and some reactions of an ammonium salt of arsenomolybdic acid. Freidheim<sup>2</sup> also gives the analysis of salts prepared by the action of molybdic anhydride on ammonium arsenate and of ammonium molybdate on ammonium arsenate.

In this work the method of treating an acid solution of ammonium molybdate with arsenic acid, and also by salting out from this solution with ammonium salt was used in the preparation.



## II

## Preparation

One hundred grams of molybdic acid were dissolved in 500 cc of 2.5/n ammonia. This solution was then very slowly added with constant stirring, to 1000 cc of 6.3/n nitric acid, the temperature of the mixture being maintained at zero degrees centigrade throughout the addition. A solution of forty grams of sodium arsenate slightly acidified with nitric acid was then added, and the mixture was heated on a water bath at from 50 to 60 degrees centigrade. Heating continued at this temperature for 24 hours produced about 25 grams of fine light yellow, crystalline precipitate which was then filtered off.

The addition of 300 grams of ammonium nitrate, which with the 50 grams (approximately) resulting from the previous neutralization, made a total of 350 grams in the two liters of solution, caused the precipitation in the course of 8 hours at the same temperature of some 50 grams of crystals. This yield was of a slightly darker yellow than that obtained previously. The further addition of 100 grams of ammonium nitrate and continued heating yielded now about 20 grams of precipitate after 8 hours. After standing several days about 10 grams more



precipitate was filtered from this same solution.

Still two more filtrations were made of this solution after it had stood in each case about one week at room temperature, and each time about 10 grams were obtained. The six yields varied in color from a light yellow ( first) to a somewhat brighter yellow( last sample). However, the variation in shade being greatest between samples one and two. It will be recalled that sample one was obtained before salting out. These samples obtained by the several filtrations were kept in separate containers in order that separate analysis of them would be possible.

In the course of the procedure it was noted that if the acid mixture from which the yellow crystals were precipitated, was slowly neutralized with ammonia, the molybdic acid would be precipitated instead of the desired product.

### III

#### Analysis

The product, after drying was examined under the microscope and found to appear homogeneous, altho the several samples differed somewhat in size of the crystals.

The following qualitative tests were made: the precipitation of magnesium ammonium arsenate by magnesia mixture indicat-





ed the presence of arsenic; warming the substance with sodium hydroxide and testing the vapor with wet litmus paper indicated the presence of the ammonium radical; reduction to various shades of blue or blue green indicated the presence of molybdenum.

A quantitative analysis for these substances was conducted as follows:

1. Determination of Arsenic content. Half gram samples of the ammonium arsenomolybdate were dissolved each in 100 cc. of water, treated with 5 cc. of concentrated hydrochloric acid. Twenty-five cc. of magnesia mixture was added, and after neutralization with 10% ammonium hydroxide, an excess of  $1/3$  the volume of the neutralized solution was added. After standing 24 hours the solution was filtered through a Gooch ( asbestos) crucible, the precipitate was washed with 2.5% ammonium hydroxide, and dried at  $100^{\circ}$  centigrade. The precipitate was then ignited in a muffle furnace up to  $900^{\circ}$  centigrade, cooled, and weighed as magnesium pyroarsenate (  $Mg_2 As_2 O_7$  )

Sample	% As	Sample	% As
1	13.74	4	—
	13.08		6.19
2	6.85	5	6.22
	7.31		6.39
3	6.78	6	5.68
	7.42		5.33

2. Determination of ammonium content.

One third gram samples were dissolved in 200 cc. of water and distilled with 25 cc. of 5% (wt) sodium hydroxide solution



previously boiled. Distillation was continued until the distillate was  $\frac{2}{3}$  the volume of the original solution. The distillate was received in 25 cc. of n/10 solution of hydrochloric acid and the excess titrated with standard sodium hydroxide.

Sample	% $\text{NH}_4$
1	2.4
	2.5
2	4.6
	4.7
3	5.1
	4.2
4	4.3
	5.0

### 3. Determination of molybdenum content.

The alkaline filtrates from the arsenic precipitations were used for the molybdenum determinations. After most of the free ammonia had been removed by heating, the filtrate was neutralized with dilute sulfuric acid and evaporated to about 100 cc. Ten cc. of dilute sulfuric acid was added and the solution placed in a 300 cc. oval pressure flask which had a porcelain top like that of a citrate of magnesia bottle. After the air in the flask was partly removed by the application of vacuum, the flask was connected with hydrogen sulfide under pressure until the solution was saturated with the gas. The stopper was then fastened and the flask placed in a water bath at a temperature of from 60 to 80 degrees centigrade for about half



an hour.

Filtration through an asbestos Gooch crucible proved inadequate as the molybdenum sulfide was partly in the colloidal state. This difficulty was overcome by heating the solution for a longer period at a slightly higher temperature ( 80 to 100 degrees for about an hour and allowing to stand over night). It was found that from three to five successive precipitations were necessary for the complete removal of the molybdenum from the solution. Incomplete removal was evident in any case by the blue color of the filtrate.

Another difficulty was now encountered in that some of the sulfide in the crucible was oxidized by the air, in the interval between filtrations, to soluble compounds which were washed through into the filtrate at the following filtration. It was realized that a quantitative separation by this method would be impossible without more elaborate equipment, either in the way of a reducing atmosphere for the precipitate, or the employment of fresh Gooch crucibles for each filtration. Thinking this inadvisable, the writer decided to employ a different method, namely; of filtering each time through a fresh quantitative filter paper.

After drying the filter, the brownish-black precipitate was removed as well as possible and preserved between watch glasses while the filter paper was burned in a weighed crucible. The precipitate was then added to the crucible and ignition to the oxide attempted. This step in the process proved unsatisfactory. The sulfide was found very prone to deflagrate and the molybdic





acid to volatilize as stated by Mellor<sup>3</sup>. A number of the precipitates were ignited and in each case it proved difficult to maintain the proper temperature, for with too small a flame the ignition was exceedingly slow, and with a slightly larger flame deflagration took place unexpectedly from time to time. Moreover, after this stage was passed it was difficult to completely convert the blue residue to the white oxide without causing some volatilization.

A third method was now tried. It was intended to ignite the precipitate with a little pure sulfur in a current of hydrogen by means of a Rose crucible<sup>4</sup>. Consequently a Kipp hydrogen generator was set up and to which was connected, a wash tower containing potassium permanganate in concentrated sulfuric acid, a wash tower containing 40 per cent sodium hydroxide solution, and also a calcium chloride drying tower. However, at this time it was found impossible to get complete precipitation of the molybdenum sulfide, as previously. It was attempted with solutions of sulfuric acid content ranging from 5 to 60 cc of the dilute acid in 150 cc. of solution, but in each case the blue color of the filtrate persisted.

A fourth method was now tried.<sup>5</sup> The arsenic was first removed as before by precipitation with magnesia mixture. The excess ammonia was neutralized with hydrochloric acid. A few drops of ammonium hydroxide were added and then 2 or 3 cc. of acetic acid ( 33 per cent) in excess and the solution diluted to 200 cc. The solution was boiled. Boiling was continued while 40 to 50 cc. of a lead acetate solution ( 40 grams of





lead acetate crystals per liter) were added and then for four more minutes accompanied with vigorous stirring. The precipitate was allowed to settle, and then was filtered thru asbestos in a Gooch crucible with suction. The precipitate was washed by decantation with a boiling solution of 25 grams of ammonium chloride and ten drops of acetic acid per liter until free from lead. The washings were tested with hydrogen sulfide for lead.

In washing by decantation, the wash solution was kept as hot as possible and the mixture stirred vigorously before each decantation. After being washed free from lead, the precipitate was washed twice with boiling water. The crucible was heated on an asbestos plate until dry and then over a free flame. It was cooled and the precipitate weighed as  $\text{Pb Mo O}_4$ .

Sample	% Mo
1	47.34
2	47.29
	48.36
3	49.42
	48.21
4	51.17
	51.34
5	46.16
	46.10

#### 4. Determination of moisture content.

For this determination samples were heated in an electric oven.



Sample	% loss at 100°C	% loss at 110°C	% loss at 150°C
1	1.27	1.77	2.38
2	4.06	5.21	6.06
3	2.87	3.70	4.53
4	1.68	2.33	3.30

### Calculations

The following calculations were made from the data obtained by the analyses in order to determine formulae, if possible:

( Percentages figured on samples as obtained)

%Mo	%MoO <sub>3</sub>	% As	% As <sub>2</sub> O <sub>5</sub>	% NH <sub>4</sub>	Total %
47.34	71.01	13.08	20.05	2.5	93.56
47.29	70.93	6.85	10.50	4.6	86.03
48.36	72.54	7.31	11.21	4.7	88.45
49.42	74.13	6.78	10.39	5.1	89.62
48.21	72.31	7.42	11.38	4.2	89.89
51.17	76.75	--	--	4.3	—
51.34	77.01	6.19	9.49	5.0	91.50
46.16	69.24	6.22	9.54	--	--
46.10	69.15	6.39	9.80	--	--

				Ratio	
%MoO <sub>3</sub> ÷ 144	%As <sub>2</sub> O <sub>5</sub> ÷ 230	%NH <sub>4</sub> ÷ 18	MoO <sub>3</sub>	As <sub>2</sub> O <sub>5</sub>	NH <sub>4</sub>
.4931	.0871	.1389	5.66	1	1.59
.4926	.0456	.2556	10.80	1	5.60
.5038	.0487	.2611	10.34	1	5.36
.5148	.0451	.2833	11.42	1	6.28
.5022	.0494	.2333	10.17	1	4.72
.5348	.0412	.2778	12.98	1	6.74



( Percentages figures on samples dried at 110°C)

%Mo	%MoO <sub>3</sub>	%As	%As <sub>2</sub> O <sub>5</sub>	%NH <sub>4</sub>	Total
48.19	72.28	13.22	20.42	2.54	95.24
49.89	74.83	7.22	11.07	4.85	90.75
51.02	76.53	7.71	11.92	4.95	93.30
51.32	76.98	7.04	10.79	5.29	93.06
56.06	75.09	7.70	11.80	4.36	91.25
52.39	78.59	--	--	--	--
52.57	78.85	6.33	9.70	5.11	93.66

Ratio

%MoO <sub>3</sub> ÷ 144	%As <sub>2</sub> O <sub>5</sub> ÷ 230	%NH <sub>4</sub> ÷ 18	MoO <sub>3</sub>	As <sub>2</sub> O <sub>5</sub>	NH <sub>4</sub>
.5020	.0887	.1411	5.65	1	1.58
.5197	.0481	.2694	10.80	1	5.59
.5315	.0514	.2750	10.34	1	5.35
.5346	.0409	.2939	11.39	1	6.26
.5215	.0513	.2422	10.16	1	4.72
.5476	.0421	.2839	12.98	1	6.70

## IV

Arseno-Molybdic Acid as a Qualitative Reagent For  
Alkaloids.

Solutions of the alkaloids quinidine, cinchonine and cinchonidine in hydrochloric acid were prepared and to each was added arsenomolybdic acid solution ( a solution of the ammonium salt in dilute hydrochloric acid) until the precipitation was complete, and then an excess added. The treatment of the clear filtrate with Mayer's reagent gave no precipitate or cloudiness



to the solution.

Samples of salts prepared in this work were heated over a wide range of temperature, starting at one hundred degrees centigrade. Color changes, were observed, which, altho not bearing directly on the subject of this work, were quite interesting. The writer has attempted to describe these color changes in tabular form, and the temperature given are approximate.

Sample	100°	105°	125°	185°	190°
1	yellow	lighter yellow	white	white to pale green	pale green
2	"	dark yellow	pale yellow	" yellow	" orange
3	"	"	orange yellow	orange	deep orange
4	"	"	"	"	deep orange

	210°	230°	250°	270°
1	pale green	pale green to brown	green brown	dark green to brown
2	orange to green	orange and green	myrtle green	myrtle green
3	orange to green	orange and green	myrtle green	myrtle green
4	orange	orange and green	dark orange and green	dark orange and green

	300°	asbestos gauze 3 in. flame	4 in. flame
1	shiny brown	deep green	shinny brown
2	green brown	yellow green	dark green
3	green brown	yellow green	dark green
4	green brown	orange green	dark green

) all  
smoke  
) and  
give  
) off  
fumes







Sample	5 in. flame	red heat	when cool
1	dark blue green	orange yellow	shinny silver white
2	moss green to blue	yellow	shinny silver white
3	moss green to blue	yellow	shinny silver white
4	moss green to blue	yellow	shinny silver white

## V

## Conclusions

It is believed that from the results of this work the following conclusions may be drawn:

1. That the ammonium salt of an arsenomolybdic acid was prepared.

2. That by treating ammonium molybdate in acid solution with sodium arsenate one complex was formed, while by salting out from the same solution a different complex was formed.

3. That of the samples prepared the first has probably one formula and the others another formula. The samples prepared were not purified and consequently from the data obtained by the analyses it is not possible to conclude definite formulae.

4. That the arsenomolybdic acids prepared, or their salts in acid solution, are quantitative precipitants for alkaloids.



## VI

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